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Ionization and Neutralization Processes

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Dissociative recombination in polyatomic ions is discussed. A new process, tidal termolecular ionic recombination has been discovered. Deactivation of $O_2(^5\Pi)$ by N_2 is discussed in connection with termolecular association of oxygen. The temperature-dependence of termolecular association has been explained. An experimentally-determined rate of $N(^2D)$ quenching by $O(^3P)$ is shown to be incompatible with forbidden-red-line observations. Transition probabilities for some O_2 bands have been computed. The $O(^1S)$ production-mechanisms, relevant to observations on the nocturnal F-region, are discussed. A review on negative ions has been written. Cross sections for photoionization of $O(2p^4 \ ^3P, \ ^1D, \ ^1S)$ $O(2p^3 3s \ ^3,^5S^o)$ and $O(2p^3 3p \ ^3,^5P)$ have been calculated by the R-matrix method. A preliminary study of photoionization of $N(2p^3 \ ^4S^o)$ has been made. R-matrix calculations of electronic excitation of N_2 by electron-impact agree well with experiment for the X→A and X→W transitions and reveal the importance of resonances, and preliminary studies of excitation of O_2 indicate reasonable agreement with experiment. An accurate R-matrix calculation

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SECTION I

A. Dissociative recombination of polyatomic ions

The key question in the context of the dissociative recombination of polyatomic ions is: What are the dissociation products? One of the factors which controls this is the occurrence of favourable crossings of potentials. It is not possible to determine theoretically whether or not there is a favourable crossing without doing very lengthy ab initio quantal computations but some relevant elementary considerations have been discovered. There are two main classes of saturated polyatomic ion. A member of the first class has a free valence or contains an ionized atom (for example C^+) the number of whose valences increases on neutralization. Breaking a bond yields radicals, and generally there are enough accessible potentials to make a crossing quite likely. A member of the second class contains an ionized atom (for example N^+ or O^+) the number of whose valences decreases on neutralization so that one of the products of breaking a bond is a saturated molecule and only a single potential is accessible. In this circumstance there is unlikely to be a favourable crossing. However in many cases a favourable crossing is to be expected for the channel in which two H atoms are shed and a H_2 molecule is formed from them. This is because of the considerable spread in the vibrational energy that may be carried by the H_2 molecule. Branching ratios cannot easily be predicted. Each depends on the product of the favourability of the crossing (as measured by the Frank-Condon factor) and the probability of the transition (D. R. Bates, Astrophys. J. 344, 531, 1989).

B. Tidal termolecular ionic recombination

A new recombination process, tidal termolecular ionic recombination, has been discovered. It arise from calculations

aimed at explaining measurements (S. P. Mezyk, R. Cooper and J.
Sherwell, J. Phys. Chem. $\underline{93}$, 8187, 1989) on processes like

$$Xe_2^+ + Cl^- + Xe \rightarrow XeCl^* + 2Xe$$
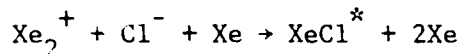
which were carried out in connection with rare gas halide lasers.
The experiments proved that the recombination coefficient is far
higher than expected. Monte Carlo simulation that allowed for the
$Cl^- - Xe^+$, $Cl^- - Xe$ and $Xe^+ - Xe$ forces showed that the rotational
and vibrational modes of Xe_2^+ tend to be excited by the passage of
Cl^- through perihelion. Because of this electrostatic tidal action
the orbit contracts and the internal energy of Xe_2^+ increases leading
to dissociation. The measured values of the recombination
coefficient have been reproduced satisfactorily (D. R. Bates and W.
Lowell Morgan (Phys. Rev. Lett. $\underline{64}$, in press 1990).

C. Deactivation of O_2 and termolecular association of oxygen

It has been shown that the rate coefficient for the deactivation
of O_2 $(^5\Pi_g)$ by N_2 is probably low enough to ensure that collisional
dissociation $O_2(^5\Pi_g) + N_2 \rightarrow 2O + N_2$ prevents the reaction $O + O + N_2$
$\rightarrow O_2(^5\Pi_g) + N_2$ from contributing appreciably to the measured total
termolecular association coefficient (D. R. Bates, Chem. Phys. Lett.
$\underline{162}$, 313, 1989).

D. Temperature dependence of termolecular association

The dependence of the rate coefficient k for termolecular
association between the diatomic ions A^+ and diatomic molecules B on
the temperature T of the ambient gas has been considered. There is
experimental evidence that k decreases rapidly as T is increased if
the association energy is small. It was shown that the required T
variation could ensue if the reactants in the energized complex AB^{+*}

repel one another at some relative orientations (D. R. Bates, J.
Chem. Phys. $\underline{90}$, 87, 1989).

E. $N(^2D)$ quenching and the forbidden red line

Theoretical considerations show that if the rate coefficient for
$N(^2D) + O(^3P) \rightarrow N(^4S) + O$ is indeed 2.8×10^{-11} cm^3 s^{-1} as measured
by L. E. Jusinski, G. Black and T. G. Slanger (J. Phys. Chem. $\underline{92}$,
5977, 1988) the product oxygen atoms must be in the ^1D state. This
is incompatible with observational data on the forbidden red line
emission. It was inferred that the $N(^2D) + O(^3P)$ quenching
measurement must have been vitiated by some factor which did not
enter a companion $N(^2D) + O_2(X)$ quenching measurement (D. R. Bates,
Planet Space Si. $\underline{37}$, 1145, 1989).

F. Transition probabilities for O_2 bands

Absolute transition probabilities have been computed for the
bands of the Herzberg I, Chamberlain, Herzberg II and Herzberg III
systems of molecular oxygen (D. R. Bates, Planet. Space Si. $\underline{37}$, 881,
1989).

G. $O(^1S)$ production and the nocturnal F-region

The $O(^1S)$ quantum yield in O_2^+ dissociative recombination $f(^1S)$
in the nocturnal F-region and processes $O^+ + O_2 \rightarrow O + O_2^+$ $(v \leq 7)$ and
$O_2^+(v) + O \rightarrow O_2^+$ $(v' < v) + O$ have been discussed. The values of
$f(^1S)$ obtained from the Visible Airglow Experiment (V. J. Abrev, S.
C. Solomon, W. E. Sharp and P. B. Hayes J. Geophys. Res. $\underline{88}$, 4140,
1983) do not seem explicable in terms of the ab initio results of
Guberman (Nature, $\underline{327}$, 408, 1987) on the $\alpha(^1S,v)$ direct dissociative
recombination coefficients. Arguments have been advanced to show
that the discrepancy cannot be attributed to an overlooked $O(^1S)$
source in the F-region. Doubt has been thrown on the correctness of
the results of the Visible Airglow Experiment by a recent
determination of the $f(^1S)/f(^1D)$ ratio by H. Takahashi, B. R.

Clemensha, P. P. Batista, Y. Sahai, M. A. Abdu and P. Muralikrishna
(Planet. Space Sci. 38, 547, 1990) from equatorial F-region profile
measurements. These are consistent in general with theoretical
expectations. However discrepancies appear in detailed facets of
the data. If they are real they may conceivably be due to the
computed $\alpha(^1S,v)$ being less accurate than has been supposed. The
possibility has been raised that $\alpha(^1S,0)$, in particular, is affected
by the neglected indirect dissociative recombination Laboratory
measurements on $f(^1S)$ by J. L. Queffelec, B. R. Rowe, F. Vallee, J.
C. Gomet and M. Morlais (J. Chem. Phys. 91, 5335, 1989) have been
considered and it has been concluded that they conflict with so much
independent evidence that they must be regarded with reserve (Dr. R.
Bates, Planet. Space Sci. 38, in press 1990).

H. Negative ions

A long review article "Negative ions: structure and spectra" has
been written (D. R. Bates, Adv. Atomic. Molec. and Optical Physics,
27, in press 1990).

PHOTOIONIZATION OF OXYGEN AND NITROGEN

A.   Oxygen

In the work performed, studies have been made for the photoionisation of the $2p^4$ ^3P, ^1D, ^1S; $3s$ $^{3,5}S^o$ and $3p$ $^{3,5}P$ states of atomic oxygen

$$h\nu + O(^3P, \, ^1D, \, ^1S, \, ^{3,5}S, \, ^{3,5}P) \rightarrow e^- + O^+.$$
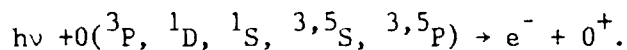
Whilst photoionisation of the $2p^4$ ^3P ground state has been investigated theoretically for the last fifty years, limited research has been carried out on the photoionisation of excited states. Indeed for all of the above excited states the theoretical work has been limited to the extent that none of it has included autoionising resonances.   An important feature of the present work is therefore the inclusion of such resonances.   Despite all of the work on the ground state, there are still several discrepancies between theory and experiment, particularly above the $^4S^o$ threshold and the $^2P^o$ threshold.   Part of this work therefore has been to improve on the calculations of Pradhan (J. Phys. B: At. Molec. Phys. 11, L729, 1978) and Taylor and Burke (J. Phys. B: At. Mol. Phys. 9, L353, 1976). These authors employed R-matrix approached and includes some O^+ target states arising from the $2s^2 2p^3$ and $2s 2p^4$ configurations.

In all of the calculations performed in this study, we employed the R-matrix method and included eleven target states of O^+: $2s^2 2p^3$ $^4S^o$, $^2D^o$, $^2P^o$; $2s 2p^4$ ^4P, ^2D, ^2S, ^2P; $2s^2 2p 3s$ ^4P, ^2P, ^2D, ^2S.   Each of these states was represented by configuration-interaction type wave functions and the energies and energy separation between levels agreed closely with experiment and represented a significant improvement on all previous calculations.

1. ^{3}P state

Figure 1 displays the present results.   The most significant

conclusion is that the theoretical data has converged and thus the

discrepancies, above the ^{4}S^o and ^{2}P^o threshold, with experiment still

remain but must almost certainly lie with the experimental

procedures.   We shall see below that the photoionisation cross

sections for the ^{1}D and ^{1}S states are dominated by a broad resonance,

the position of which lies in the region above the ^{2}P^o threshold.   A

possible explanation therefore of the discrepancy above the ^{2}P^o

threshold is that there may exist excited states of atomic oxygen in

the experimental beam.   However, we note that this is not applicable

to experiment of Hussein et al (J. Phys. B: At. MOl. Phys. $\underline{18}$, 2827,

1985).

2. ^{1}D, ^{1}S states

Figures 2 and 3 display the present results.   The wide

divergence among previous results is clearly apparent.   The

significant discovery of the present study is the occurrence of a

broad 2s2p^5 ^{1}P^o Coster-Kronig resonance in both the ^{1}D and ^{1}S state

photoionisaton cross sections.

3.   3s ^{3,5}S^o and 3p ^{3,5}P states

The only theoretical work available for these states is that of

Saxon et al (Phys. Rev. $\underline{A39}$, 1156, 1989) for the 3p^{3}P state.   Their

work did reveal the interesting feature of a Cooper minimum in the

O$^+$(^{4}S^o)εd ^{3}D^o final channel, but did not include allowance for

autoionising resonaces.   Thus, the present work is not only the sole

data available for the 3s ^{3,5}S^o and 3p ^{5}P states (very limited

experimental data exists) but is the most sophisticated for all

states.   Cooper minima was found for both the 3p ^{3}P and 3p ^{5}P states

and careful analysis using oscillator strengths for neutral oxygen

was performed to confirm both the accuracy of the present calculation

and hence the position of the Cooper minima. For the $2p^3 3s$ $^{3,5}S^o$

states it was found that the photoionisation cross sections are

dominated at high energies by the contributions arising from ejection

of a 2p electron (the 3s behaving like a 'spectator' electron).

Two papers have occurred from the above work:

Photoionisation of the $2p^4$ ^3P, ^1D, ^1S states of atomic oxygen,

K. L. Bell, P. G. Burke, A. Hibbert and A. E. Kingston,

J. Phys. B: At. Mol. Opt. Phys. 22, 3197, 1989.

Photoionisation of the $2p^3 3s$ $^{3,5}S^o$, $2p^3 3p$ $^{3,5}P$ states of atomic

oxygen,

K. L. Bell, K. A. Berrington, P. G. Burke, A. Hibbert and A. E.

Kingston.

J. Phys. B: At. Mol. Opt. Phys. (in press, 1990).

B. Nitrogen

A preliminary study of the photoionisation of the ground $^4S^o$

state of atomic nitrogen has been carried out. The R-matrix method

was used and nine target states of N^+ have been included in the

calculation: $2s^2 2p^2$ ^3P; $2s2p^3$ $^5S^o$, $^3D^o$, $^3P^o$, $^3S^o$; $2s^2 2p3s$ $^3P^o$;

$2s^2 2p3p$ ^3D, ^3S, ^3P. The results are found to differ little from the

less sophisticated work of Le Dournuef et al (J. Phys. B: At. Mol.

Phys. 12, 2449, 1979). The study however is being continued by

attempting to obtain better representation of the above target

states. The continuation is important since recent experimental

data (Samson and Angel, private communication) differs significantly
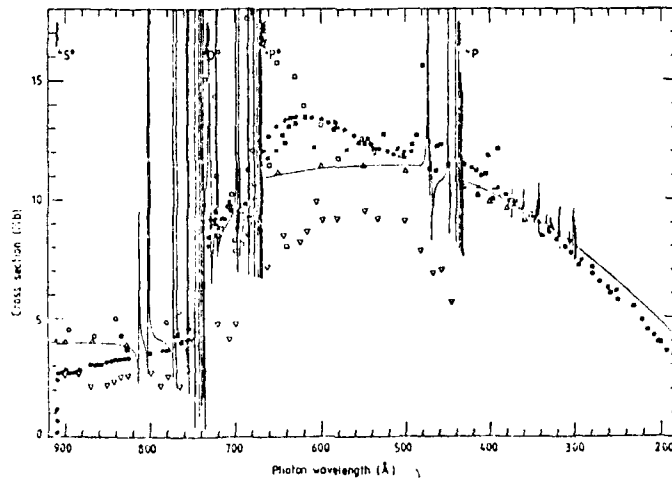
from the theoretical results.

Figure 1. Photoionisation cross section of the ^3P state of atomic oxygen. Theory: ——, present results, △, Pradhan (1978); ×, Taylor and Burke (1976). Experiment. ▽, Comes et al (1968); ○, Kohl et al (1978); □, Hussein et al (1985), ■, Samson and Pareek (1985); ●, Angel and Samson (1988). (Thresholds correspond to experimental values.)
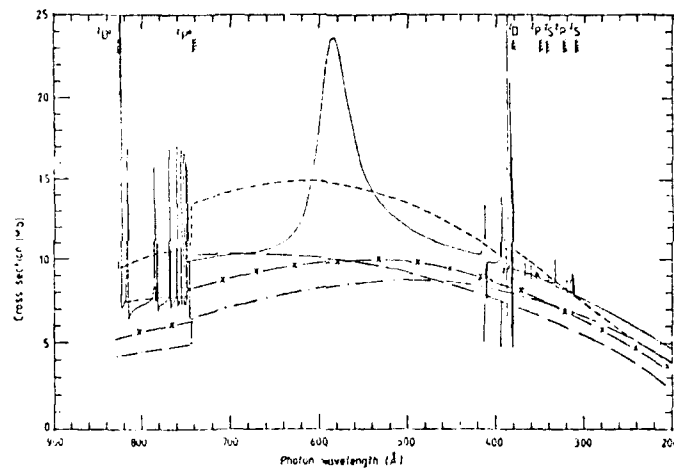

Figure 2. Photoionisation cross section of the ^1D state of atomic oxygen. ——, present results, – · –, (length), — —, (velocity), Henry (1967); – × –, Thomas and Helliwell (1970), – – –, Koppel (1971). (Thresholds correspond to experimental values.)

Figure 3. Photoionisation cross section of the ^1S state of atomic oxygen ——, present results, – · –, (length), — —, (velocity), Henry (1967); – × –, Thomas and Helliwell (1970), – – –, Koppel (1971). (Thresholds correspond to experimental values.)
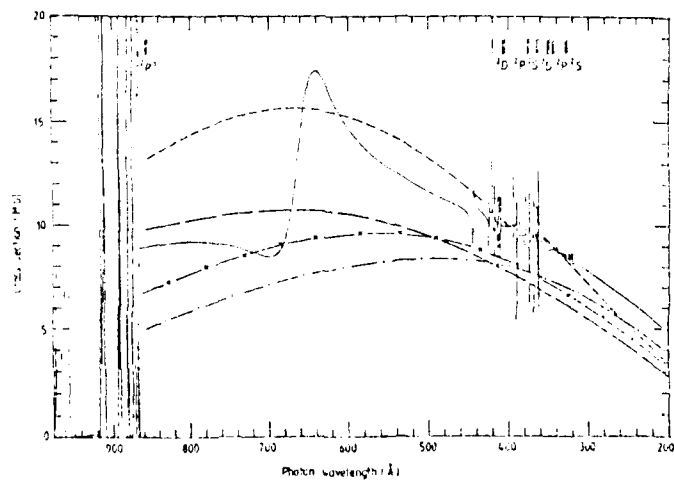
ELECTRON MOLECULE COLLISIONS

In the past decade many calculations have been reported on low-energy collisions of electrons with diatomic molecules allowing for rotational and vibrational excitation in the electronic ground state. It is now possible to obtain accurate cross sections for these processes and at Queen's University of Belfast work has been carried out on a number of molecules including N_2, HF and HCl using the R-matrix method.

By comparison, little work has been carried out on the process of electronic excitation of the target, although such processes, particularly in the cases of N_2 and O_2, are urgently required in many applications. The only exception to this is work on electronic excitation of H_2, where calculations for exciting the $^3\Sigma_u^+$ state carried out using the R-matrix method were in good agreement with calculations using the linear algebraic equations method and the Schwinger variational method.

However in the last year a detailed program of work has been initiated at Queen's University Belfast to calculate accurate electronic excitation cross sections for N_2 and O_2 using the R-matrix method. In the case of N_2, attention has initially been focussed on transitions from the X $^1\Sigma_g^+$ ground state to the first three low lying valence excited states of the molecule A $^3\Sigma_u^+$, B $^3\Pi_g$ and W $^3\Delta_u$. Also, for the first time in electron molecule collisions, CI wave functions were used to represent the target states which is important in order to obtain accurate energy spacings and transition moments. The results show that these cross sections are dominated by resonances over the first 10 eV. Good agreement is obtained with experiment for the X $\rightarrow$ A and X $\rightarrow$ W transitions but further work needs to be carried out to include more target states and to include the nuclear motion which has been neglected in these preliminary

calculations.   This work is described in the paper: C. J. Gillan, C.
J. Noble and P. G. Burke: Electronic excitation in low energy
electron scattering by N_2 molecules.   J. Phys. B: At. Mol. Opt.
Phys. to be published.

Work on O_2 is also well underway involving a collaboration
between Queen's University Belfast and the Daresbury Laboratory.   In
this case, nine target states arising from the configurations $1\pi_u^4$
$1f_g^2$ and $1\pi_u^3 1\pi_g^3$ are being included in the calculation and interest
is focussed on transitions from the X $^3\Sigma_g^-$ ground state to the first
two electronically excited states $^1\Delta_g$ and b $^1\Sigma_g^+$.   Preliminary
results indicating reasonable agreement with experiment have been
obtained.   This work will be submitted for publication in the near
future.

It is intended to continue the program of work on electronic
excitation of N_2 and O_2.   The nuclear motion will be included in the
calculations and transitions involving both electronic and
vibrational excitation will be studied.

DIELECTRONIC RECOMBINATION

Recent accurate calculations on the photoionization of atomic oxygen carried out at Queen's University Belfast by Bell et al (1989, referred to above) raised the prospect of obtaining, for the first time, accurate dielectronic recombination rates given by

$$e^- + 0^+(2s^2\ 2p^3\ ^4S^o) \rightleftharpoons 0^*(n\ell) \rightarrow 0^1 + h\nu$$
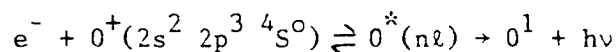
where 0^* is a resonance state and 0^1 an excited bound state of the oxygen atom. Over the last six months, therefore, these earlier R-matrix photoionisation calculations have been extended in this way by Terao et al. It has been found that the rate coefficients are about one half of those obtained by Badwell and Pindzola (1989) using a less accurate distorted wave method, with a maximum value of 3 x 10^{-12} cm^3 sec^{-1} at an electron temperature of about 10 eV. This work is described in the forthcoming paper: M. Terao, K. L. Bell, P. G. Burke and A. Hibbert: Theoretical study of dielectronic recombination of 0^+. J. Phys. B: At. Mol. Opt. Phys. submitted